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⑮ Process for producing poly(allylamine) derivatives.

⑯ Poly(allylamine salt) of high polymerization degree is obtained in high yield by the polymerization of monoallylamine salt with a specified radical-polymerization initiator having in the molecule an azo group. Various poly(allylamine) derivatives are obtained by reacting said poly(allylamine salt) with cyanic acid salts, acrylic compounds, or formic acid and formaldehyde.

PROCESS FOR PRODUCING POLY(ALLYLAMINE) DERIVATIVES

1 BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to a process for producing poly(allylamine) derivatives. More particularly, it relates 5 to the procedures for producing poly(allylurea), reaction product of poly(allylamine) and an acrylic compound, and poly(N-methylated allylamine).

DESCRIPTION OF THE PRIOR ART

i. Being a cationic polymer having a primary 10 amino group, poly(allylamine) would be supposed to be highly reactive and to react with various compounds. Accordingly, if it is actually possible to introduce various substituent groups into poly(allylamine) by the reaction with various compounds, there will be provided a means to modify the 15 properties of poly(allylamine) so as to meet the requirements of a particular use. This will be of industrial significance. It has, however, been not easy to obtain poly(allylamine) itself which is the starting material to prepare derivatives by the introduction of various groups.

20 In the presence of common polymerization initiators, allylamine polymerizes to a polymer of low polymerization degree in a low yield. A poly(allylamine) of high polymerization degree is obtained only by the radiation polymerization. For several reasons, however, the radiation 25 polymerization is not a technique accessible to anyone who

1 desires to utilize it. Therefore, it has been difficult
to produce on a commercial scale poly(allylamine) and, in
turn, poly(allylamine) derivatives.

ii. Further, for instance, it is predictable
5 from its structure that poly(allylurea), one of the poly-
(allylamine) derivatives, will exhibit an ability to form
a strong hydrogen bond and, by virtue of this property,
would find various uses including the use as a flocculant.
However, when it is tried to polymerize allylurea, there is
10 obtained only a polymer of too low a polymerization degree
and in too low a yield to be of a practical value. It is
possible to obtain a poly(allylurea) of high polymerization
degree by polymerizing allylamine by use of the radiation
polymerization technique and reacting the poly(allylamine)
15 with a cyanate salt to effect carbamoylation. This process,
however, is not practicable owing to the radiation poly-
merization technique which is difficult to carry out on
a commercial scale. Therefore, development of a commercial
process for producing poly(allylurea) has been awaited.

20 iii. Further, for instance, the primary amino
group of poly(allylamine) is expected to undergo addition
reaction with a compound having an unsaturated bond
adjacent to an electron attracting group. Thus, when poly-
(allylamine) is reacted with acrylonitrile, cyanoethylation
25 is expected to take place, resulting in introduction of
highly polar cyano group into poly(allylamine); when reacted
with acrylamide, there will occur carbamoylethylation,
resulting in introduction of carbamoyl group capable of

1 forming a strong hydrogen bond; when reacted with sodium
salt of acrylic acid, there will occur carboxyethylation,
resulting in introduction of negative charge; and when
reacted with an acrylic ester, there will occur introduc-
5 tion of a hydrophobic group into poly(allylamine). However,
as described above, since poly(allylamine) is obtainable
only by a very specific polymerization technique, there has
heretofore been no commercial process for producing poly-
(allylamine) derivatives by the reaction with acrylic
10 compounds. Therefor, such a commericial process has been
strongly demanded to be available.

iv. Further, poly(N-methylated allylamine) is
also expected to find several uses. However, when
monomeric N-methylallylamine or N-dimethylallylamine is
15 polymerized in the presence of common radical-polymeriza-
tion initiators, there is obtained only a trace amount of
low-molecular-weight poly(N-methylallylamine) or poly-
(N,N-dimethylallylamine). A process for producing
poly(N-methylated allylamine) by the N-methylation of
20 poly(allylamine) is conceivable but not commercially
practicable, because, as described above, high-molecular-
weight poly(allylamine) is obtained only by the specific
technique of radiation polymerization. Therefor, the
development of a commrecially feasible process has been
25 awaited.

SUMMARY OF THE INVENTION

i. Under the circumstances described above, the

1 present inventors carried out an extensive study to develop a practicable process for producing poly(allylurea) and, as a result, found that poly(allylurea) is obtained in high yields by polymerizing an inorganic acid salt of monoallylamine with a radical-polymerization initiator having an azo group in the molecule to produce a poly(allylamine salt) in high yields, and reacting the resulting poly(allylamine salt) with a cyanic acid salt. The present invention is predicated upon this discovery.

5 10 The present invention is to provide a process for producing poly(allylurea), which comprises polymerizing a mono-allylamine salt with a radical-polymerization initiator having an azo group in the molecule, and allowing the resulting poly(allylamine salt) to react with a salt of

15 cyanic acid.

ii. Further, the present inventors carried out an extensive study to develop a practicable process for producing poly(allylamine) derivatives which are expected to be formed by the reaction between poly(allylamine) and acrylic compounds and, as a result, found that the intended derivatives can be formed by converting the high-molecular-weight poly(allylamine salt) obtained above in a high yield into poly(allylamine), and allowing the resulting poly(allylamine) to react with acrylic compounds. This

20 25 invention is predicated upon this discovery. This invention provides a process for producing poly(allylamine) derivatives by polymerizing an inorganic acid salt of monoallylamine with a radical-polymerization initiator

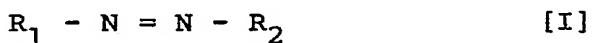
1 having an azo group in the molecule, converting the resulting poly(allylamine salt) into poly(allylamine), and reacting the latter with acrylic compounds.

iii. Further, the present inventors carried out
5 an extensive study to develop a practicable process for producing poly(N-methylallylamine) and poly(N,N-dimethyl-allylamine) and, as a result, found that poly(N-methylated allylamine) is obtained in high yields by allowing the poly(allylamine salt) obtained above in a high yield or the
10 poly(allylamine) obtained therefrom by the action of an alkali to react with formic acid and formaldehyde. This invention is predicated upon this discovery. The present invention provides a process for producing poly(N-methylated allylamine), which comprises polymerizing an inorganic acid
15 salt of monoallylamine with a radical-polymerization initiator having an azo group in the molecule, and allowing the resulting poly(allylamine salt) or the poly(allylamine) obtained therefrom by the action of an alkali to react with formic acid and formaldehyde to produce poly(N-
20 methylated allylamine) in high yields. The present invention is predicated upon this discovery. The present invention provides a process for producing poly(N-methylated allylamine), which comprises polymerizing an inorganic acid salt of monoallylamine with a radical-polymerization
25 initiator having an azo group in the molecule, and allowing the resulting poly(allylamine salt) or the poly(allylamine) obtained therefrom by the action of an alkali to react with formic acid and formaldehyde.

1 DETAILED DESCRIPTION OF THE INVENTION

i. In the present process for producing poly-(allylamine) derivatives including poly(allylurea), derivatives of poly(allylamine) derived by the reaction 5 with acrylic compounds, and poly(N-methylated allylamine), at first poly(allylamine salt) is produced by polymerizing an inorganic acid salts of monoallylamine with a polymerization initiator. The initiators used according to this invention are those having an azo group in the molecule.

10 Typical examples are salts of the azo compounds represent by the following general formula [I] with inorganic or organic acids such as hydrochloric acid, sulfuric acid, phosphoric acid, alkylsulfuric acids, p-toluenesulfonic acid, formic acid, acetic acid, and propionic acid:



15 wherein at least one, preferably both, of R_1 and R_2 is a group which contains a cationizable nitrogen atom and which is selected from the group consisting of aminoalkyl, aminoaryl, amidinylalkyl, amidinylaryl, aminoalkaryl, aminoaralkyl, amidinylaralkyl, amidinylalkaryl, cyanoaminoalkyl, 20 and cyanoaminoalkaryl; when only one of R_1 and R_2 is a group containing a cationizable nitrogen atom, the other is a group selected from the group consisting of alkyl, aryl, alkaryl, aralkyl, cyanoalkyl, cyanoaryl, cyanoalkaryl, and cyanoaralkyl; and R_1 and R_2 may jointly form a single 25 alkylene group represented by the general formula



1 wherein R is a group selected from the group consisting of alkylene, alkylalkylene, and arylalkylene; covalent bonds (a) and (b) combine with each nitrogen atom of the azo group to form an azo-containing ring; and X is a group containing
5 a cationizable nitrogen atom.

Of the initiators represented by the general formula [I], especially preferred are those having a secondary or tertiary carbon atom adjacent to the azo group. Typical of such compounds are as given below.

10 2,2'-Diamidinyl-2,2'-azopropane hydrochloride,
2,2'-diamidinyl-2,2'-azobutane hydrochloride, 2,2'-diamidinyl-2,2'-azopentane hydrochloride, 2,2-bis(N-phenylamidinyl)-2,2'-azopropane hydrochloride, 2,2'-bis(N-phenylamidinyl)-2,2'-azobutane hydrochloride, 2,2'-bis(N,N-dimethylamidinyl)-2,2'-azopropane hydrochloride,
15 2,2'-bis(N,N-dimethylamidinyl)-2,2'-azobutane hydrochloride,
2,2'-bis(N,N-diethylamidinyl)-2,2'-azopropane hydrochloride,
2,2'-bis(N,N-diethylamidinyl)-2,2'-azobutane hydrochloride,
2,2'-bis(N-n-butylamidinyl)-2,2'-azopropane hydrochloride,
20 2,2'-bis(N-n-butylamidinyl)-2,2'-azobutane hydrochloride,
3,3'-bis(N,N-di-n-butylamidinyl)-3,3'-azopentane
hydrochloride, azo-bis-N,N'-dimethyleneisobutyl-amidine
hydrochloride.

Azonitriles of the quaternary ammonium salt type
25 obtained by quaternizing, by means of dimethyl sulfate or

1 methyl p-toluenesulfonate, such compounds as 2,2'-azobis-
2 (2-methyl-4-diethylamino)butyronitrile hydrochloride, 2,2'-
azobis (2-methyl-4-dimethylamino)butyronitrile hydrochloride,
2,2'-azobis (2-methyl-4-diethyl-amino)butyronitrile
5 hydrochloride, 2,2'-azobis (2-methyl-4-diethylamino)-
butyronitrile, or 2,2'-azobis (2-methyl-4-dimethylamino)-
butyronitrile.

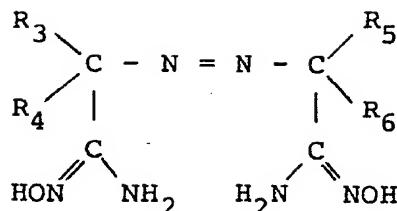
3,5-Diamidinyl-1,2-diazo-1-cyclopentene hydro-
chloride, 3-methyl-3,4-diamidinyl-1,2-diazo-1-cyclopentene
10 hydrochloride, 3-ethyl-3,5-diamidinyl-1,2-diazo-1-cyclo-
pentene hydrochloride, 3,5-dimethyl-3,5-diamidinyl-1,2-
diazo-1-cyclopentene hydrochloride, 3,6-diamidinyl-1,2-
diazo-1-cyclohexene hydrochloride, 3-phenyl-3,5-diamidinyl-
1,2-diazo-1-cyclopentene hydrochloride, 3,5-diphenyl-3,5-
15 diamidinyl-1,2-diazo-1-cyclopentene hydrochloride.

Since the process for polymerizing an inorganic
acid salt of monoallylamine in the presence of an inorganic
or organic acid salt of the azo compounds represented by
the general formula [I] has been disclosed in our copending
20 European patent application No. 83301719.7 (publication No.

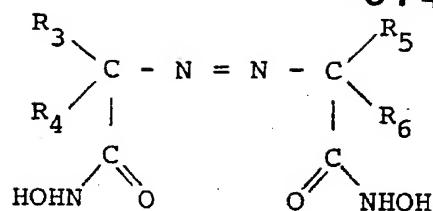
0 095 233), details are omitted from
the present specification.

Other typical examples of the initiators used
in the polymerization of monoallylamine salts according
25 to this invention are those represented by the following
general formula [III] or [IV]:

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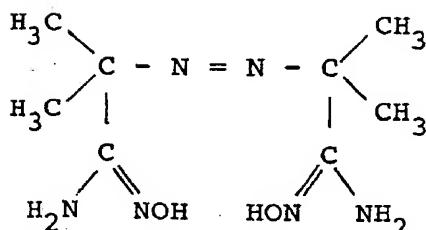
[III]



[IV]

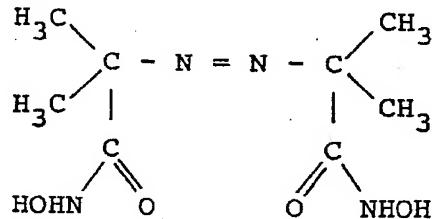
1 wherein R₃, R₄, R₅ and R₆ are the same or different hydrocarbon radicals. Specially preferred hydrocarbon radicals, R₃, R₄, R₅ and R₆, are straight- or branched-chain alkyls having 1 to 4 carbon atoms, cycloalkyls having 5 to 6 carbon atoms, phenyl, and benzyl. R₃ and R₄ or/and R₅ and R₆ jointly with carbon atoms, to which the hydrocarbon radicals are attached, may form a ring. Especially preferred initiators of the formulas [III] and [IV] are as follows:

[III]

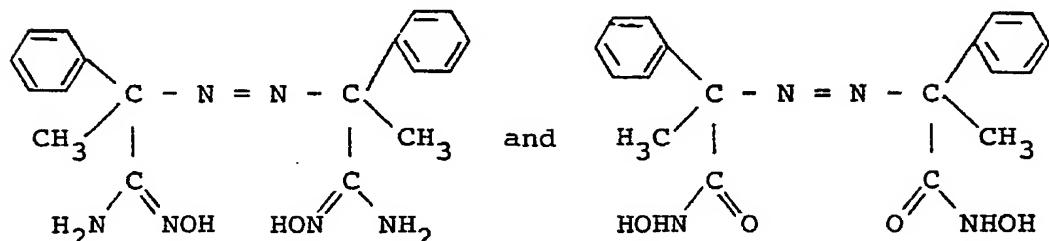
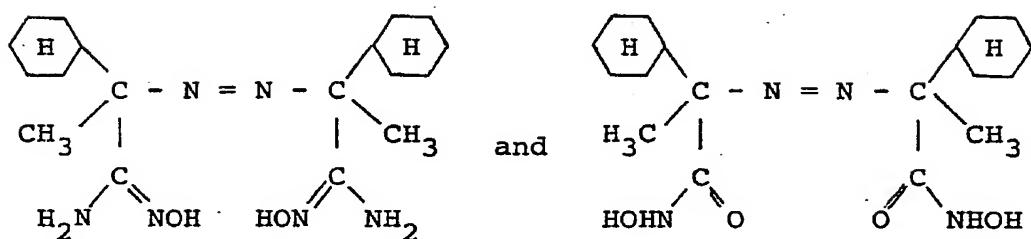
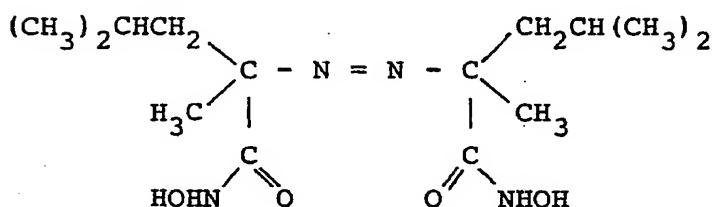
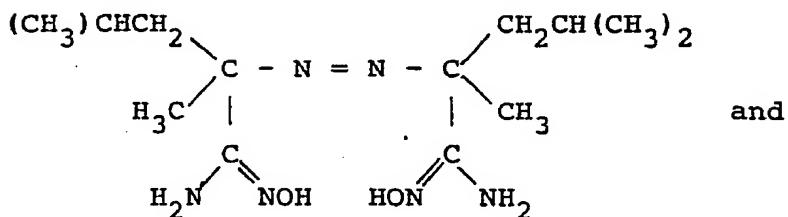
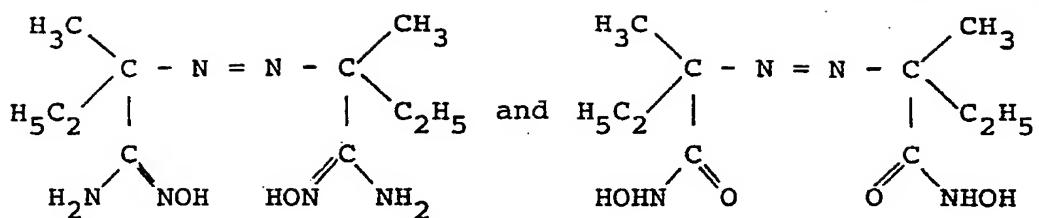


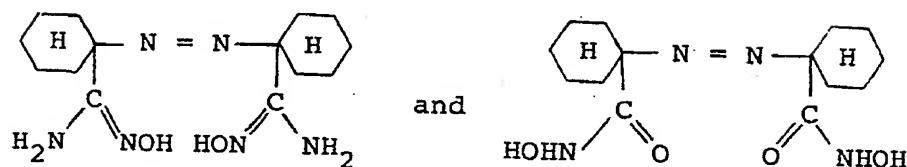
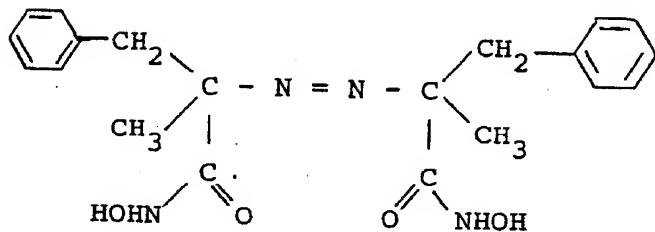
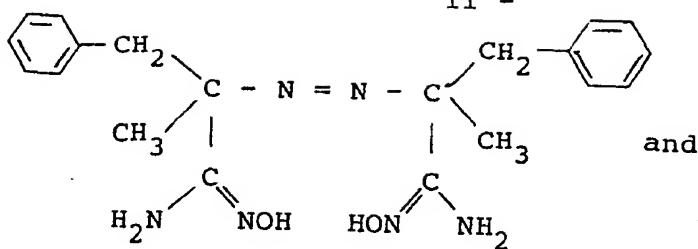
2,2'-Azobis(2-methyl-
propioamidoxime)

[IV]



2,2'-Azobis(2-methyl-
propionhydroxamic acid)





1 It is needless to say that the invention is not limited to these examples.

The process for polymerizing an inorganic acid salt of monoallylamine by using as initiator a compound 5 of the general formula [III] or [IV] is disclosed by the present inventors in Japanese Patent Application, "A process for producing polymerized monoallylamine" (application date: Nov. 10, 1983).

The amount used of an intiator is 0.1 to 10, 10 usually 1 to 6, % by weight based on the inorganic acid salt of monoallylamine. The polymerization temperature is 30° to 100°C, usually 40° to 70°C, depending upon the chemical structure of the initiator. The initial monomer

1 concentration is higher the better within the solubility
range. The concentration is usually 10 to 85% by weight.
Preferable inorganic acid salts of monoallylamine are
hydrochloride, sulfate, sulfite, and phosphate. The
5 polymerization is carried out in polar solvents such as
water, inorganic acids (e.g. hydrochloric acid, sulfuric
acid, phosphoric acid, and polyphosphoric acid), aqueous
solutions thereof, organic acids (e.g. formic acid,
acetic acid, propionic acid, lactic acid, etc.), aqueous
10 solutions thereof, alcohols, dimethyl sulfoxide, dimethyl-
formamide, or aqueous solutions of inorganic salts (e.g.
zinc chloride, calcium chloride, and magnesium chloride).

In carrying out the polymerization, although
the inorganic acid salt of monoallylamine is used usually
15 in the form of crystals separated from the mother liquor,
yet it can be used in the form of solution in which the
salt has been produced by the addition of monoallylamine
and an inorganic acid to the polar solvent. When the
inorganic acid or an aqueous solution thereof is used
20 as the polymerization medium, it is of course possible
to add a predetermined quantity of monoallylamine to the
inorganic acid or the aqueous solution thereof and to
allow the polymerization to take place in the resulting
solution. The polymerization is carried out preferably
25 in an inert gas such as nitrogen, because the atmospheric
oxygen hinders the polymerization to some degrees.

ii. The procedure of preparing poly(allylurea)
by the reaction between the poly(allylamine salt)

1 obtained above and a cyanate salt is described below.

The poly(allylamine salt) can be used either as a solution obtained by the above-mentioned polymerization procedure or after precipitation from the solution 5 by the addition of a large amount of methanol followed successively by filtration, drying, and dissolution in water. When poly(allylamine salt) of higher molecular weight is required, the molecular weight can be increased by the action of a bifunctional reagent such as an 10 epihalohydrin or ethylene dichloride to cause partial crosslinking.

A 5- to 50-% solution of poly(allylamine salt) dissolved in water or a polar solvent is heated at 30°C to 80°C. After dropwise addition of an aqueous solution of 15 a cyanate salt (e.g. potassium or sodium cyanate), the resulting mixture is allowed to react for 10 to 20 hours. If necessary, the by-product salt [potassium chloride when poly(allylamine hydrochloride) is reacted with potassium cyanate] is removed by subjecting the reaction 20 mixture to dialysis, ultrafiltration, or gel permeation.

iii. The preparation of poly(allylamine) derivatives by the reaction between the poly(allylamine salt) and an acrylic compound is carried out in the following manner:

25 At first, an aqueous solution of the poly(allylamine salt) is allowed to react with equimolar amount of a strong alkali such as sodium hydroxide. The reaction mixture is subjected to dialysis,

1 ultrafiltration, or gel permeation to remove the by-
product salt [sodium chloride when poly(allylamine
hydrochloride) and sodium hydroxide were used], then
dehydrated, and dried to yield poly(allylamine).
5 Poly(allylamine) derivatives are obtained by reacting
the resulting poly(allylamine) with acrylic compounds
having an electron attracting group adjacent to the double
bond, such as, for example, acrylonitrile, metha-
crylonitrile, acrylamide, methacrylamide, acrylic acid,
10 methacrylic acid, acrylic esters, methacrylic esters,
inorganic acid salts of acrylic acid, and inorganic acid
salt of methacrylic acid. The detailed description of
the procedure is given below.

The poly(allylamine) is dissolved in water,
15 methanol, or a mixture of a polar solvent and water or
methanol to a concentration of 5 to 60%. To the solution,
while being kept at 20°C or below, is added dropwise an
acrylic compound as such (when liquid) or dissolved in
water or methanol (when solid). The amount of the
20 acrylic compound can be varied within the range from 0.1
to 200 mole-% of poly(allylamine). After completion of
the dropwise addition, the mixture is stirred for about
2 hours, then at 40° to 50°C for 1 to 2 hours to allow
the reaction to complete.

25 The flow chart of the preparation of poly-
(allylamine) derivatives according to this invention is
as follows:

Solution of monoallylamine salt

↓ Polymerization (1)

Solution of poly(allylamine salt)

↓ Precipitation with
methanol (2)

Poly(allylamine salt)

↓ Strong alkali (3)

Solution of poly(allylamine) and salt

↓ Salt removal (4)

Solution of poly(allylamine)

↓ Drying (5)

Poly(allylamine)

↓ Dissolution (6)

Solution of poly(allylamine)

↓ Reaction with
acrylic compound (7)

Solution of poly(allylamine) reacted
with acrylic compound

↓ Precipitation with
acetone (8)

Poly(allylamine) reacted with acrylic
compound

1 In the above process, step (2) of precipitation
with methanol, step (4) of salt removal, step (5) of
drying, step (6) of dissolution, and step (8) of precipi-
tation with acetone may be omitted according to cir-
5 cumstances.

iv. In the preparation of poly(N-methylated
allylamine) according to this invention poly(allylamine
salt) can be used as such or after conversion into

1 poly(allylamine). Poly(allylamine) is obtained in the
following manner:

Poly(allylamine salt) is dissolved in water
and mixed with equimolar amount of a strong alkali such
5 as sodium hydroxide. The by-product salt (sodium
chloride when monoallylamine hydrochloride and sodium
hydroxide were used) is removed from the reaction mixture
by dialysis, ultrafiltration; or gel permeation. The
dialyzate or filtrate is then dehydrated and dried. The
10 procedure of preparing poly(N-methylallylamine) or
poly(N,N-dimethylallylamine) by reacting the resulting
poly(allylamine) or a salt thereof with formic acid and
formaldehyde is as described below.

Poly(allylamine) or a salt thereof is dissolved
15 in water or methanol or a mixture of a polar solvent and
water or methanol. The concentration of the resulting
solution is 5 to 60%. To the solution, while being kept
at 30°C or below by cooling, is added dropwise formic acid
followed by an aqueous solution of formaldehyde. In the
20 case of poly(N-methylallylamine), the necessary amounts
of formic acid and formaldehyde are 1.5 to 4 moles of
the former and 1 to 1.5 moles of the latter for 1 mole
of poly(allylamine) in terms of allylamine. In the case
of poly(N,N-dimethylallylamine), the necessary amounts
25 of formic acid and formaldehyde are 3 to 8 moles of the
former and 2 to 3 moles of the latter. The degree of
methylation can be controlled by varying the amounts of
formic acid and formaldehyde.

1 After the addition of formic acid and formaldehyde, the temperature of the mixture is elevated gradually to 70° to 90°C. Carbon dioxide is evolved vigorously. After the mixture has been kept at the
5 same temperature for 4 to 6 hours, the gas evolution ceases when the reaction is deemed to be complete. After completion of the reaction, a large volume of acetone is added to precipitate the poly(N-methylated allylamine). The precipitate is collected by filtration
10 to remove the unreacted formaldehyde and formic acid, then dried to yield formic acid salt of poly(N-methylallylamine) or poly(N,N-dimethylallylamine). If necessary, the formic acid salt is converted into free poly(N-methylallylamine) or poly(N,N-dimethylallylamine).
15 The invention is further illustrated with reference to examples.

EXAMPLE 1 Preparation of poly(allylurea)

To 57.1 g of monoallylamine, was added dropwise, at 10°-20°C, 104.2 g of 35-% hydrochloric acid to yield an aqueous solution containing 59.1% of monoallylamine hydrochloride. The resulting aqueous solution was concentrated in a rotary evaporator to a concentration of 75%. To the concentrated solution, while being maintained at 60°C by heating, was added dropwise over a period of 3 hours a 15-% aqueous solution containing 2.34 g (2.5% by weight based on the monomer) of 2,2'-diamidinyl-2,2'-azopropane hydrochloride. After

1 completion of the dropwise addition, the mixture was
kept at 60°C for 15 hours to complete the polymerization.
The polymerization mixture was poured into a large volume
of methanol to precipitate the polymer. The polymer was
5 collected by filtration and dried to yield 86 g (92%
yield) of the polymer which showed an intrinsic viscosity
of 0.32 at 30°C in N/10 aqueous sodium chloride solution.
A 20 g portion (0.214 mole in terms of monoallylamine)
of the resulting poly(allylamine hydrochloride) was
10 dissolved in 80 g of water. To the resulting solution,
while being heated at 50°C, was added dropwise an aqueous
solution containing 17.3 g (0.214 mole) of potassium
cyanate dissolved in 25 g of water. The mixture was kept
at the same temperature for 20 hours. After completion
15 of the reaction, the reaction mixture was dialyzed
against water through hollow fibers for 24 hours at 50°C
to remove the by-product potassium chloride. The
dialyzate was concentrated to 100 g, precipitated with
acetone, collected by filtration, and dried to yield
20 18.4 g of a polymer. Upon colloidal titration and acid-
alkali titration, the polymer was found to be completely
non-cationic, indicating quantitative progress of the
reaction.

EXAMPLES 2 to 4 Preparation of poly(allylurea)

25 In a manner similar to that in Example 1, the
same poly(allylamine hydrochloride) as used in Example 1
was allowed to react with varying amounts of potassium

1 cyanate as shown in Table 1.

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Table 1

Example No.	Poly(allylamine) g (mole)	Potassium cyanate g (mole)	Yield g	Degree of carbamoylation * %
2	20.0 (0.214)	12.1 (0.150)	18.7	69
3	20.0 (0.214)	8.67 (0.107)	19.0	50
4	20.0 (0.214)	5.20 (0.0641)	17.6	29

Note: * As determined by colloidal titration.

It is seen from Table 1 that the reaction proceeded nearly quantitatively in each case.

EXAMPLE 5 Preparation of poly(allylurea)

5 An equal amount of water was added to 37.4 g of poly(allylamine hydrochloride) (intrinsic viscosity of 0.30 in N/10 aqueous sodium chloride solution at 30°C) prepared by the polymerization in a manner similar to that in Example 1. To the resulting solution, were 10 added 36 g (90 mole-%) of a 40-% aqueous sodium hydroxide solution and 0.148 g (0.4 mole-%) of epichlorohydrin. The mixture was heated at 50°C for 30 hours, while the reaction system gradually became viscous. The reaction mixture was added to methanol to precipitate 37 g of a 15 polymer having an intrinsic viscosity of 1.4 in N/10 aqueous sodium chloride solution at 30°C. A 20 g portion

1 of the polymer was reacted with 17.3 g of potassium cyanate to effect carbamoylation. The yield was 19.7 g and the carbamoylation degree was 98 %.

EXAMPLE 6 Preparation of reaction product between
5 poly(allylamine) and acrylic compound.

An aqueous solution containing 59.1% of mono-allylamine hydrochloride was prepared by adding dropwise 104.2 g of 35-% hydrochloric acid to 57.1 g of monoallylamine at 10° to 20°C. The resulting solution was concentrated in a rotary evaporator to a concentration of 75%. To the concentrated solution maintained at 60°C, was added dropwise over a period of 3 hours a 15-% aqueous solution containing 2.34 g (2.5 % by weight based on the monomer) of 2,2'-diamidinyl-2,2'-azopropane hydrochloride. After completion of the addition, the mixture was kept at 60°C for 15 hours. After completion of the polymerization, the polymerization mixture was poured into a large volume of methanol to precipitate a polymer. The polymer was collected by filtration and dried. The yield was 86 g.

An aqueous solution was prepared by adding 30 g of water to 20 g of the poly(allylamine hydrochloride) obtained above. To the resulting solution, was added 21.4 g of 40-% sodium hydroxide solution. The mixture was dialyzed through hollow fibers for 24 hours to remove the by-product sodium chloride. The dialyzed solution was concentrated to 100 g and lyophilized to yield 11.6 g

1 of poly(allylamine). A 11.4 g portion (0.2 mole in terms
of allylamine) of the poly(allylamine) was dissolved in
30 g of methanol. To the resulting solution, while being
maintained at 20°C or below, was added dropwise 10.6 g
5 (0.2 mole) of acrylonitrile, while slight evolution of
heat being noticed. After completion of the addition,
the mixture was kept at the same temperature for 2 hours.
The mixture was then heated at 40°C for 2 hours to
complete the reaction. The reaction mixture was poured
10 into a large volume of acetone to precipitate the reac-
tion product. After being collected by filtration and
dried, the precipitate gave the following results of
elementary analysis:

	C%	H%	N%
Found	65.93	9.12	24.95
Calculated*	65.42	9.15	25.43

Note: The values calculated on the assumption that
one molecule of acrylonitrile had added to
each amino group of poly(allylamine).

From the above results and the results of
15 analysis of IR absorption spectrum (strong absorption at
2,260 cm^{-1} corresponding to the nitrile group) and
 $^1\text{H-NMR}$ spectrum, it may be concluded that the reaction
product is a polymer formed by the addition of one
molecule of acrylonitrile to each amino group of
20 poly(allylamine).

1 EXAMPLE 7 Preparation of reaction product between poly-
(allylamine) and acrylic compound.

To a solution of 11.4 g of poly(allylamine), - obtained as in Example 6, in 30 g of methanol, while 5 being maintained at 20°C or below, was added dropwise a solution of 14.2 g (0.2 mole) of acrylamide in 20 g of methanol. Slight evolution of heat was noticed. After completion of the addition, the mixture was kept at the same temperature for 2 hours, then at 40°C for 2 hours 10 to allow the reaction to complete. The reaction mixture was poured into a large volume of acetone to precipitate the reaction product. After being collected by filtration and dried, the precipitate gave the following results of elementary analysis:

	C%	H%	N%
Found	56.34	9.50	21.97
Calculated*	56.22	9.44	21.85

Note: The values calculated on the assumption that one molecule of acrylamide had added to each amino group of poly(allylamine).

15 From the above results together with the result of analysis of the IR absorption spectrum (strong absorption at 1,670 cm^{-1} corresponding to the carbonyl group in the amide linkage) and $^1\text{H-NMR}$ spectrum, it may be concluded that the reaction product is a polymer 20 formed by the addition of one molecule of acrylamide to each amino group of poly(allylamine).

1 EXAMPLE 8 Preparation of reaction product between poly(allylamine) and acrylic compound.

To a solution of 11.4 g of poly(allylamine), which was obtained as in Example 6, in 30 g of water, 5 while being maintained at 20°C or below, was added dropwise a solution of 18.8 g (0.2 mole) of sodium acrylate in 30 g of water, meanwhile mild evolution of heat having been noticed. After completion of the addition, the mixture was kept at the same temperature for 10 2 hours, then at 40°C for 2 hours to allow the reaction to complete. The reaction mixture was poured into a large volume of acetone to precipitate the reaction product. After having been collected by filtration and dried, the precipitate gave the following results of 15 elementary analysis:

	C%	H%	N%
Found	48.01	6.71	9.43
Calculated*	47.68	6.67	9.27

Note: * The values calculated on the assumption that one molecule of sodium acrylate had added to each amino group of poly(allylamine).

From the above results together with the results of analysis of the IR absorption spectrum and ¹H-NMR spectrum, it may be concluded that the reaction product is a polymer formed by the addition of one 20 molecule of sodium acrylate to each amino group of poly(allylamine).

1 EXAMPLE 9 Preparation of reaction product bewteen
poly(allylamine) and acrylic compound.

To a solution of 11.4 g of poly(allylamine), which was obtained as in Example 6, in 30 g of methanol, 5 while being maintained at 20°C or below, was added dropwise 17.2 g (0.2 mole) of methyl acrylate, meanwhile slight evolution of heat having been noticed. After completion of the addition, the mixture was kept at the same temperature for 2 hours, then at 40°C for 2 hours 10 to allow the reaction to complete. A large volume of acetone was added to the reaction mixture to precipitate the reaction product. After having been collected by filtration and dried, the precipitate gave the following results of elementary analysis:

	C%	H%	N%
Found	59.11	9.30	9.85
Calculated *	58.72	9.15	9.78

Note: * The values calculated on the assumption that one molecule of methyl acrylate had added to each amino group of poly(allylamine).

15 From the above results together with the results of analysis of the IR absorption spectrum and ¹H-NMR spectrum, it may be concluded that the reaction product is a polymer formed by the addition of one molecule of methyl acrylate to each amino group of poly(allylamine).

1 EXAMPLE 10 Preparation of poly(N-methylated allylamine).

To 57.1 g of allylamine, was added dropwise, at 10°-20°C, 104.2 g of 35-% hydrochloric acid to yield an aqueous solution containing 59.1 % of allylamine hydrochloride. The resulting aqueous solution was concentrated in a rotary evaporator to a concentration of 75%. To the concentrated solution, while being maintained at 60°C by heating, was added dropwise over a period of 3 hours a 15-% aqueous solution containing 2.34 g (2.5% based on monomer) of 2,2'-diamidinyl-2,2'-azopropane hydrochloride. After completion of the dropwise addition, the mixture was kept at 60°C for 15 hours to complete the polymerization. The polymerization mixture was poured into a large volume of methanol to precipitate the polymer which was then collected by filtration and dried. The yield was 86 g.

A 20 g portion of the resulting poly(allylamine hydrochloride) was dissolved in 30 g of water. To the resulting solution, was added 21.4 g of a 40-% aqueous sodium hydroxide solution. The mixture was dialyzed through hollow fibers for 24 hours to remove the by-produce sodium chloride. The dialyzed solution was concentrated to 100 g and lyophilized to yield 11.6 g of poly(allylamine). To a solution of 11.4 g (0.2 mole in terms of allylamine) of the resulting poly(allylamine) in 30 g water, while being maintained at 30°C or below, was added dropwise 40.9 g (0.8 mole) of 90-% formic acid followed by 37.7 g (0.44 mole) of

1 35-% aqueous formaldehyde solution. After the addition,
the mixture was gradually heated to 80°C, meanwhile
violent evolution of carbon dioxide having been noticed.
The mixture was kept at 80°C for 5 hours when the gas
5 liberation had ceased to occur, indicating the completion
of reaction. The reaction mixture was poured into a
large volume of acetone to precipitate the reaction
product which was then collected by filtration and dried
to yield 24.2 g of a white powder. Upon elementary
10 analysis, this powder gave the following results:

	C%	H%	N%
Found	55.10	9.91	10.44
Calculated *	54.94	9.99	10.68

Note: * Calculated for formic acid salt of poly-
(N,N-dimethylallylamine).

Also from the analysis of $^1\text{H-NMR}$ spectrum,
the polymer was confirmed to be poly(N,N-dimethyl-
allylamine).

EXAMPLE 11 Preparation of poly(N-methylated allylamine).

15 In a manner similar to that in Example 10,
11.4 g of poly(allylamine), which was prepared as in
Example 10, was reacted with 20.5 g (0.4 mole) of 90-%
formic acid and 18.9 g (0.22 mole) of 35-% formalin to
yield 22.0 g of the reaction product. Upon elementary
20 analysis, this substance gave the following results:

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	C%	H%	N%
Found	50.73	9.18	12.24
Calculated *	51.26	9.47	11.96

Note: * Calculated for formic acid salt of poly-
(N-methylallylamine).

1 Also from the analysis of $^1\text{H-NMR}$ spectrum, the
polymer was confirmed to be poly(N-methylallylamine).

WHAT IS CLAIMED IS:

1. A process for producing a poly(allylurea), which comprises polymerizing an inorganic acid salt of monoallylamine with a radical-polymerization initiator having an azo group in the molecule, and allowing the resulting poly(allylamine salt) to react with a cyanic acid salt.
2. A process according to claim 1, wherein the radical-polymerization initiator having an azo group in the molecule is a salt of an azo compound represented by the following general formula [I] with an inorganic or organic acid selected from the group consisting of hydrochloric acid, sulfuric acid, phosphoric acid, alkylsulfuric acids, p-toluenesulfonic acid, formic acid, acetic acid, and propionic acid:



[I]

wherein at least one, preferably both, of R_1 and R_2 is a group which contains a cationizable nitrogen atom and which is selected from the group consisting of aminoalkyl, aminoaryl, amidinylalkyl, amidinylaryl, aminoalkaryl, aminoaralkyl, amidinylaralkyl, amidinylalkaryl, cyanoaminoalkyl, and cyanoaminoalkaryl; when only one of R_1 and R_2 is a group containing a cationizable nitrogen atom, the other is a group selected from the group consisting of alkyl, aryl, alkaryl, aralkyl, cyanoalkyl, cyanoaryl, cyanoalkaryl, and cyanoaralkyl; and R_1 and R_2

may jointly form a single alkylene group represented by the general formula

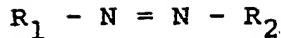


wherein R is a group selected from the group consisting of alkylene, alkylalkylene, and arylalkylene; covalent bonds (a) and (b) combine with each nitrogen atom of the azo group to form an azo-containing ring; and X is a group containing a cationizable nitrogen atom.

3. A process according to Claim 1, wherein the cyanic acid salt is potassium or sodium cyanate.

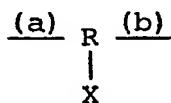
4. A process for producing a poly(allylamine) derivative, which comprises polymerizing an inorganic acid salt of monoallylamine with a radical-polymerization initiator having an azo group in the molecule, converting the resulting poly(allylamine salt) into poly(allylamine), and allowing the resulting poly(allylamine) to react with an acrylic compound.

5. A process according to Claim 4, wherein the radical-polymerization initiator having an azo group in the molecule is a salt of an azo compound represented by the following general formula [I] with an inorganic or organic acid selected from the group consisting of hydrochloric acid, sulfuric acid, phosphoric acid, alkylsulfuric acids, p-toluenesulfonic acid, formic acid, acetic acid, and propionic acid:



[I]

wherein at least one, preferably both, of R_1 and R_2 is a group which contains a cationizable nitrogen atom and which is selected from the group consisting of aminoalkyl, aminoaryl, amidinylalkyl, amidinylaryl, aminoalkaryl, aminoaralkyl, amidinylaralkyl, amidinylalkaryl, cyanoaminoalkyl, and cyanoaminoalkaryl; when only one of R_1 and R_2 is a group containing a cationizable nitrogen atom, the other is a group selected from the group consisting of alkyl, aryl, alkaryl, aralkyl, cyanoalkyl, cyanoaryl, cyanoalkaryl, and cyanoaralkyl; and R_1 and R_2 may jointly form a single alkylene group represented by the general formula



[II]

wherein R is a group selected from the group consisting of alkylene, alkylalkylene, and arylalkylene; covalent bonds (a) and (b) combine with each nitrogen atom of the azo group to form an azo-containing ring; and X is a group containing a cationizable nitrogen atom.

6. A process according to Claim 4, wherein the acrylic compound is selected from the group consisting of acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, acrylic acid, methacrylic acid, acrylic esters, methacrylic esters, inorganic acid salts of acrylic acid,

and inorganic acid salts of methacrylic acid.

7. A process for producing a poly(N-methylated allylamine), which comprises polymerizing an inorganic acid salt of monoallylamine with a radical-polymerization initiator having an azo group in the molecule, and allowing the resulting poly(allylamine salt) or the poly(allylamine) derived therefrom by the action of an alkali to react with formic acid and formaldehyde.

8. A process according to Claim 7, wherein the radical-polymerization initiator having an azo group in the molecule is a salt of an azo compound represented by the following general formula [I] with an inorganic or organic acid selected from the group consisting of hydrochloric acid, sulfuric acid, phosphoric acid, alkylsulfuric acids, p-toluenesulfonic acid, formic acid, acetic acid, and propionic acid:



wherein at least one, preferably both, of R_1 and R_2 is a group which contains a cationizable nitrogen atom and which is selected from the group consisting of aminoalkyl, aminoaryl, amidinylalkyl, amidinylaryl, aminoalkaryl, aminoaralkyl, amidinylaralkyl, amidinylalkaryl, cyanoaminoalkyl, and cyanoaminoalkaryl; when only one of R_1 and R_2 is a group containing a cationizable nitrogen atom, the other is a group selected from the group consisting of alkyl, aryl, alkaryl, aralkyl, cyanoalkyl, cyanoaryl, cyanoalkaryl, and cyanoaralkyl;

and R_1 and R_2 may jointly form a single alkylene group represented by the general formula



wherein R is a group selected from the group consisting of alkylene, alkylalkylene, and arylalkylene; covalent bonds (a) and (b) combine with each nitrogen atom of the azo group to form an azo-containing ring; and X is a group containing a cationizable nitrogen atom.